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A New Room-Temperature Molten Salt Electrolyte

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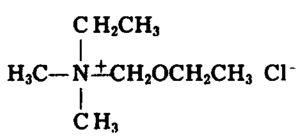
The evaluation of room-temperature molten salt systems as suitable electrolytes for battery applications is a subject of ongoing research in our laboratory. Several room-temperature molten salt systems have been reported (1-4). One of particular interest to us has been the 1-methyl-3-ethylimidazolium chloride (MEIC)/$AlCl_3$ system (3). These melts are described in terms of their apparent mole fraction, N, of $AlCl_3$. Melts with $N < 0.5$ are basic due to the presence of the Cl^- anion, and melts with $N > 0.5$ are acidic due to the presence of the $Al_2Cl_7^-$ anion. In basic melts, the anodic limit is the oxidation of chloride ions and the cathodic limit the reduction of the organic cation resulting in an electrochemical window of approximately 3V (5). The only two metals found to form reversible couples in the basic melts are gallium, at elevated temperatures, and cadmium at ambient temperatures. By increasing the electrochemical window of such a melt, one could increase the amount of reversible couples, thus increasing the number of materials which could be used as cathodes in a battery.

Based on its similarity to a series of compounds reported by Angell (6), we chose to study a mixture of a tetraalkylammonium chloride salt and aluminum chloride.



*Electrochemical Society Active Member.

The tetraalkylammonium chloride salt chosen was dimethylethylethoxymethyl ammonium chloride ($N_{211\ 102}Cl$). The tetraalkylammonium chloride is described by a numerical designation in which the ones and twos refer to the number of carbon atoms in the alkyl side chains attached to the central nitrogen atom. When an oxygen atom is encountered in the side chain, an "O" is added to the number and the numbers on either side denote the carbon atoms adjacent to the oxygen (as in the "102" designation for the ethoxymethyl group in $N_{211\ 102}Cl$).

Experimental

The $N_{211\ 102}Cl$ is prepared by dropwise addition of dimethylethylamine to chloromethylethyl ether at 25°C with diethyl ether as the solvent. The reaction is run for 4h. The solvent is removed by cannula and the product dried under vacuum. The yield is 90% with no further purification needed. The addition of $AlCl_3$ to $N_{211\ 102}Cl$ causes an exothermic reaction to occur, similar to the MEIC/$AlCl_3$ molten salt system. The heat generated in the mixing process can lead to decomposition of the melt; therefore, to prepare a melt, the aluminum chloride was added slowly to the $N_{211\ 102}Cl$. Melts in which the apparent mole fraction, N, of $AlCl_3$ was ≥ 0.5 decomposed, giving off ethyl chloride. Ethyl chloride was identified by sampling the headspace above the melt with a gas-tight syringe followed by analysis by gas chromatography-mass spectrometry (GC/MS). Therefore, only melts with an apparent mole fraction $AlCl_3$ of less than 0.5 were studied. The GC/MS analysis was carried out on a Hewlett Packard (Palo Alto, California) 5985

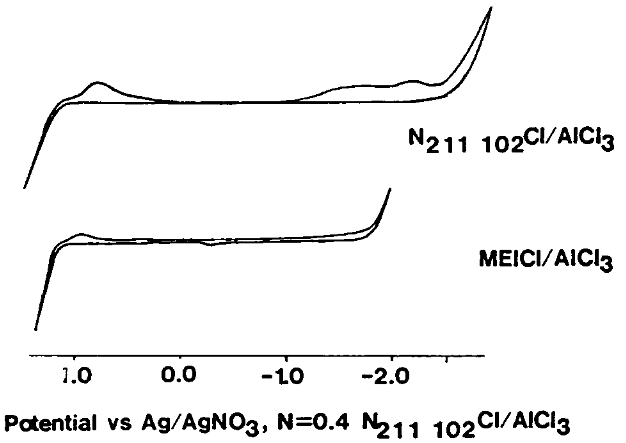


Fig. 1. Comparison of electrochemical windows between basic $AlCl_3$/MEIC and $AlCl_3$/$N_{211\ 102}Cl$ melts. The working electrode was Pt and the counterelectrode was Mo.

GC/MS system. Cyclic voltammetry was carried out using an EG&G PAR (Princeton, New Jersey) Model 173 potentiostat/galvanostat with a Model 175 universal programmer. All melts were prepared and cyclic voltammetry done in a glove box (Vacuum Atmospheres, Hawthorne, California) under a helium (99.999%) atmosphere.

Results and Discussion

The electrochemical window of an $N = 0.40$ $AlCl_3/N_{211\ 102}Cl$ melt is shown in Fig. 1. The cathodic limit appears to be the reduction of the organic cation, and the anodic limit the oxidation of Cl^-, which is similar to the MEIC/$AlCl_3$ system. A series of working electrodes, including tungsten, aluminum, zinc, glassy carbon, and platinum were tested in the new melt system. No aluminum deposition occurred at any of the working electrodes, with the cathodic limit being the irreversible reduction of the organic cation. The anodic limit of the aluminum and zinc electrode was the irreversible oxidation of the metal into the melt. A series of chloride salts, including magnesium, lithium, zinc, and cadmium, were added to the melt, and the electrochemical window scanned on platinum and glassy carbon working electrodes. No electrochemical activity was seen for the magnesium, lithium, or zinc chlorides. Cadmium showed reversible behavior similar to that observed in the MEIC/$AlCl_3$ system. A comparison of the two melt systems, Fig. 1, shows a wider electrochemical window by 0.7V for the $N_{211\ 102}Cl/AlCl_3$ system than for the MEIC/$AlCl_3$ system due to the lower reduction potential for $N_{211\ 102}$ cation.

The reduction waves at −2.2 and −1.8V were not explored further. Based on our experiences with other room temperature molten salt systems, these waves are most likely due to organic impurities encountered in the synthesis and traces of water from the acetonitrile used to recrystallize the organic salt. The ^{27}Al nuclear magnetic resonance images for several compositions of the melt show the predominant Al species to be $AlCl_4^-$. This is also similar to the MEIC/$AlCl_3$ system. The inability to plate aluminum from basic melts of either system is probably due to the stability of the $AlCl_4^-$ anion. The specific conductance of the new melt system was also studied. Compared with melts of similar compositions of the MEIC/$AlCl_3$ system (7), the new melt systems' specific conductance is lower by a factor of four. Like the MEIC/$AlCl_3$ system, the specific conductance of $N_{211\ 102}Cl/AlCl_3$ melts increases upon the addition of benzene.

Conclusion

The new room-temperature molten salt system described has a wider electrochemical window and lower specific conductance than the MEIC/$AlCl_3$ system. The presence of the $AlCl_4^-$ anion is common to basic compositions of the two melt systems, as is the electrochemical behavior of certain metals and metal halides. No further work is planned on this system.

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